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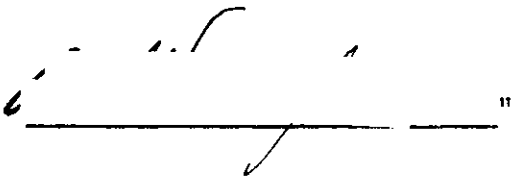

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CATALYTIC HYDROGENATION STUDIES USING FIVE PER CENT RHODIUM SUPPORTED CATALYSTS

A THESIS

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by

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SUMMARY

A catalyst of five per cent rhodium supported on alumina has been used to effect the hydrogenation of 15 ketones, including both straight and branched chain aliphatic and cyclic ketones. It was shown that the reductions produced the corresponding alcohols as the only product.

Standard reaction mixtures of 0.0274 mole ketone, 1.000 g. catalyst, and 50 ml. of acetic acid were hydrogenated at 64.7 p.s.i.a. and 25° C., and it was observed that the reaction could be followed as a function of the hydrogen pressure. The amount of ketone remaining at any time, t, could be calculated from the pressure drop via the general gas law. A plot of $(C_o - x)$, where C_o was the initial amount of ketone added and x was the amount reacted at t, versus t was linear with a slope of $K/2.303$, K being the reaction rate constant. This corresponded to reaction kinetics of first order in ketone; however, when reactions were run with twice and one-half of the standard amount of ketone, the reaction rate constant changed. By use of the Noyes equation and the half-lives of these hydrogenations, the reaction was shown to be 0.6 order with respect to ketone.

The reaction rate constant varied as the initial hydrogen pressure was changed from the standard value: at 32.3 p.s.i.a. a reaction rate constant of one-half that at 64.7 p.s.i.a. was obtained. This is in agreement with the concept that the reaction is first order in hydrogen. Since the drop in hydrogen pressure within a single run is small

in comparison with the drop in ketone concentration, the absence of a term for hydrogen in the kinetic expression for a single run is expected.

The reaction rate constant and the weight of catalyst used were in direct proportion over the range of from about 0.5 g. to 3.0 g.

An Arrhenius type temperature dependence of the reaction rate with temperature was found, and the activation energies were calculated from the slope of the $\log K$ versus $1/T$ plots. (See table on page ix.).

From the table it is obvious that as the ketone becomes more complex, K_{30}, the reaction constant at 30° C., decreases. Two possible causes are apparent: steric hindrance to adsorption at the catalyst surface; and steric hindrance to the approach of a hydrogen molecule to a catalyst site adjacent to an adsorbed ketone molecule. It is believed that this latter effect is the predominant one.

Since the configurations of the straight chain methyl ketones are all quite similar in the immediate vicinity of the carbonyl group, the decrease in rate observed can not be due to differences in adsorption at the catalyst surface. Therefore, the decrease in the reaction rate constant with increasing ketone complexity is attributed to hindrance to the approach of hydrogen. If the assumption that the adsorbed ketone has a structure more like the product than the unadsorbed ketone is allowed, then it is apparent that if a methyl group be substituted for one of the α-hydrogens of acetone, the methyl group would occupy a position above the adsorbed molecule and away from the catalyst. In this position, any substituent could block the approach of hydrogen to an adjacent catalyst site; and the larger the group, the greater would be the blocking effect.

The Reduction Ketones over Five Per Cent Rhodium Supported on Alumina

Ketone	Activation Energy Calories per Mole	K_{30}, $min.^{-1}g.^{-1}$
Acetone	7,190	0.0988
Methyl ethyl	4,240	0.0794
Methyl n-propyl	6,350	0.0686
Methyl n-butyl	7,250	0.0668
Methyl n-amyl	6,040	0.0599
Methyl n-hexyl	6,010	0.0503
Methyl n-heptyl	4,570	0.0483
Methyl n-octyl	6,260	0.0476
Methyl n-nonyl	3,620	0.0479
Diethyl	6,340	0.0657
Ethyl n-butyl	6,380	0.0502
Methyl iso-propyl	11,100	0.0102
Methyl iso-butyl	10,400	0.0178
Cyclopentanone	8,300	0.116
Cyclohexanone	8,300	0.101

Hydrogen would not affect the ability of the carbon to which it is attached to rotate about the axis to the carbonyl group. If one or two α-hydrogens were then replaced by methyl groups this rotation would be greatly hindered. So long as rotation is possible the hindering group can move "out of the way" of the approaching hydrogen molecule but when it is prevented, the reaction rate would be expected to decrease sharply as is observed with methyl iso-propyl ketone.

The two cyclic ketones were found to hydrogenate more readily than acetone. This effect was considered due to the restraint on the positioning of the α-hydrogen atoms caused by the cyclic structure. Thus, in cyclopentanone the hydrogens are held in a position corresponding to rotation of the groups out of the way of approaching hydrogen, while in cyclohexanone this is true to a lesser extent.

Dow Corning Stopcock Grease was shown to act as a poison for the catalyst. Water had no effect on the reaction velocity in amounts of up to two per cent. The reduction of ketones on this catalyst was found to occur 50 per cent faster in acetic acid than in ethanol. Platinum black was ineffective under the same conditions where rhodium worked efficiently.

CHAPTER I

INTRODUCTION

The purpose of this study was to determine the reaction rate constants for the hydrogenation of a series of ketones in the presence of a catalyst composed of five per cent rhodium supported on alumina. In conjunction with this, the structure of the ketone was varied, and the effect on the reaction rate constant was studied.

Equilibrium is a thermodynamically controlled property which depends only upon the difference in the free energies of the reactants and products. Thus, a catalyst can not influence the position of an equilibrium. As a result a catalyst has been defined as "a substance which, by its presence in a medium where a reaction takes place, either increases or decreases the reaction velocity without being changed itself or appearing in the compound resulting from the reaction" (1). The manner in which the catalyst takes part in the reaction, however, is not so easily explained. While catalytic action may be broadly classified as homogeneous or heterogeneous types, inasmuch as this study deals with heterogeneous catalytic reactions, a discussion of this type of catalytic action is in order.

If one considers a system composed of a catalyst, a hydrogen acceptor dissolved in a solvent, and an atmosphere of hydrogen, one can visualize several distinct problems. First, the hydrogen must dissolve in

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(1) H. M. Lohse, Catalytic Chemistry, Chemical Publishing Co., New York, 1945, p. 1.

the solvent. This is usually facilitated by some sort of agitation which in some measure may exert control on the rate of the reaction. Second, the hydrogen and the acceptor must reach the catalyst surface and be adsorbed on it in a position favorable for reaction. Third, after the reaction has taken place, it is necessary that the products of the reaction be removed or be desorbed from the catalyst.

Each of these steps may proceed in a variety of ways. The first is affected by exposure of the solvent to the hydrogen. The second is partially a translational problem which is affected by the viscosity of the solvent and partially a problem of adsorption, which is affected by the surface area of the catalyst, the nature of the catalyst surface, and other factors which will be discussed in greater detail below. The last step is necessary because the catalyst must be able to react with many starting molecules in successive steps unless the catalyst is present is sufficient quantity to allow simultaneous reaction of all of the molecules of acceptor and hydrogen.

Adsorption on the catalyst surface appears to be the primary difference in a catalytic and a noncatalytic reaction. In heterolytic catalytic hydrogenations, adsorption usually occurs between the components of a solution and the solid catalyst. Two types of adsorption occur: physical adsorption and chemisorption.

Physical adsorption is a relatively weak adsorption and is due to van der Waals forces. Physical adsorption is essentially nonspecific with respect to adsorbent and adsorbate, easily reversible, and involves

relatively small heats of adsorption similar in magnitude to heats of liquifaction (2). This heat of adsorption is frequently found to be of the order of a few hundred calories per mole and thus physical adsorption is deemed to have little importance in heterogeneous catalytic reactions.

Chemisorption, or activated adsorption as it is sometimes called, is the result of binding by valence forces of the same nature as those which bind atoms together in molecules (3). These forces are much stronger than those involved in physical adsorption and the heats involved are of the same order as the heats of chemical reactions. Values of 10 to 100 kcal. per mole are common. For example, the energy of adsorption of a hydrogen molecule on tungsten is known to be of the order of 45 kcal. per mole at 25° C. (4). Chemisorption is irreversible or reversible only with difficulty. A high degree of selectivity is observed: one portion of a molecule may be adsorbed while the remainder is unaffected.

Chemisorption is distinguished by three factors. First, the chemisorbed layer can be only a unimolecular layer. Second, the process of chemisorption may often have an appreciable activation energy, and hence may be a slow process. Third, there is often a variance in the adsorptive capacities of the surface atoms. Thus, one speaks of active

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(2) P. H. Emmet, Ed., Catalysis, Vol. 1, Reinhold Publishing Corp., New York, 1954, p. 2.

(3) Ibid., p. 75.

(4) O. Beeck, Rev. Modern Phys., 17, 61 (1945).

sites. Taylor (5,6) conceived the catalyst surface as consisting of unsaturated atoms more or less loosely held to the lattice structure and haphazardly distributed on the surface. These unsaturated atoms may have a varied number of free valences, depending on their relative position to other metal atoms. Such peak atoms were considered to be the seat of the catalytic activity of the surface and were called active centers. Atoms occurring on the edges of crystals were also supposed to be more active than those on plane surfaces. Taylor's ideas have been modified (7,8) and now an active center is thought to be a type of lattice defect on the surface of the metal. These lattice defects are visualized as constantly being created and destroyed with the movement of excited electrons in the lattice.

The large forces and the high degree of selectivity encountered in chemisorption may preclude the desired reaction. Thus, a variety of substances may interfere with the reaction by being strongly and preferentially adsorbed on the catalyst surface, thereby excluding the adsorption of the reactants and preventing the reaction from taking place. Such materials are called poisons. Care must be taken to remove all impurities from the reactants and the apparatus must be kept free of materials which are known to be poisons.

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(5) H. S. Taylor, Proc. Roy. Soc. (London), A-108, 105 (1925).

(6) H. S. Taylor, J. Phys. Chem., 30, 145 (1926).

(7) Emmet , op. cit., p. 85.

(8) M. Boudart, Chem. Eng. Prog., 57, No. 8, 31 (1961).

Hydrogenations using rhodium as the catalyst have employed the metal as a colloidal dispersion (9,10,11), a thin film (12), and supported on pumice, carbon, and alumina. Rhodium black has also been used. Rhodium has been used to effect the reduction of aromatic systems, heterocyclic systems, carbon-carbon double and triple bonds, free radicals, cyclopropane, nitro groups, nitrile groups, carbonyl groups, oximes, and nitric acid.

Amano and Parravano (13) have shown that a catalyst of five per cent rhodium supported on 1/16 in. alumina pellets is effective in the vapor phase reduction of benzene. They found an activation energy of 12 kcal. per mole for the reduction, and they concluded that the slow step of the reaction was the chemisorption of hydrogen.

Sabatier and Reid (14) reduced toluene to methyl cyclohexane using rhodium black as the catalyst.

The work of Gilman and Cohn (15) corroborates the usefulness of rhodium as a catalyst for the reduction of a benzene nucleus. They

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(9) C. Zenghelis and E. Stathis, Compt. rend., 206, 628 (1938), C. A., 32, 4060 (1938).

(10) C. Zenghelis and E. Stathis, Monatsh. Chem., 72,58 (1938), C. A., 32, 6934 (1938).

(11) G. Kahl and E. Biesalski, Z. anorg. u. allgem. Chem., 230, 88 (1936), C. A. 31, 3371 (1937).

(12) C. Kemball and C. T. H. Staddart, Proc. Roy. Soc., (London), A-246, 521 (1958).

(13) A. Amano and G. Parravano in A. Farkas, Ed., Advances in Catalysis, Vol. IX, Academic Press Inc., New York, 1957, p. 716.

(14) P. Sabatier and E. M. Reid, Catalysis in Organic Chemistry, D. van Nostrand Co., New York, 1923, p. 205.

(15) G. Gilman and G. Cohn in A. Farkas, Ed., Advances in Catalysis, Vol. IX, Academic Press Inc., New York, 1957, p. 733.

successfully reduced hydroquinone, β-naphthol, benzoic acid, pyrrole, quinoline, phenol, pyrogallic acid, anisole, and variously substituted derivatives of the above. Of special interest is the observation that, of the substituted benzoic acids, the ortho substituted acids were reduced slowest.

Stump (16) compared five per cent rhodium on alumina to platinum as a catalyst for the reduction of hydroxybenzenes. Reduction with platinum resulted in a large amount of cleavage of the -OH group from the ring whereas the corresponding reduction with rhodium produced little cleavage and resulted in the desired hydroxycyclohexanes.

Smith and Thompson (17,18) studied the reduction of methoxybenzenes using rhodium metal, alumina-supported rhodium, and platinum catalysts. Their work showed that supported rhodium was a better catalyst than pure rhodium based on the weight of the metal present in each. The activation energy for the reduction using all the rhodium catalysts was greater than that for the platinum catalyzed reaction. Platinum led to extensive cleavage of the carbon-oxygen bond adjacent to the ring, but hydrogenation with rhodium produced very little cleaved product.

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(16) B. L. Stump, The Catalytic Hydrogenation of Hydroxybenzenes over Platinum and Rhodium Catalysts--Kinetics of the Acid-Catalyzed Hydrolysis of the Dimethyl Esters of Cyclohexanedicarboxylic Acids, Unpublished Ph. D. Thesis, University of Tennessee, 1959, Dissertation Abstracts, 20, 1197 (1959).

(17) H. A. Smith and R. G. Thompson in A. Farkas, Ed., Advances in Catalysis, Vol. IX, Academic Press Inc., New York, 1957, p. 727.

(18) R. G. Thompson, A Study of the Catalytic Hydrogenation of Methoxybenzenes over Pt and Rh Catalysts, Unpublished Ph. D. Thesis, University of Tennessee, 1956, Dissertation Abstracts, 16, 2043 (1956).

Anisole, veratrole, hydroquinone dimethyl ether, and 1,2,3-trimethoxybenzene were reduced with negligible cleavage by five per cent rhodium on alumina.

Friedman, Doak, and Petit (19) reduced the aromatic ring in a number of organo-phosphorus compounds. Aryl phosphonic acids and diphenylphosphonic acids were reduced to the corresponding cyclohexyl derivatives by rhodium on alumina and 60 p. s. i. g. hydrogen. Halogens were cleaved from the ring. Phenyl phosphinic, benzene arsonic acid, and triphenyl bismuth could not be reduced under these conditions.

Liska and Salerni (20) reduced ethyl 5,6-benzocoumarin-3-carboxylate to the corresponding decahydronaphthalene compound using five per cent rhodium on alumina. The same catalyst has been used to reduce resorcinol to dihydroresorcinol (21).

The phenyl ring of methyl 4-amino-2-hydroxybenzoate has been reported to be hydrogenated at 50° C. over a carbon supported rhodium catalyst in acetic acid solution (22).

Carbon-carbon multiple linkages may also be reduced by rhodium. Sabatier and Reid (23) used rhodium black to reduce cinnamic acid step-

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(19) L. D. Freidman, G. O. Doak, and E. L. Petit, J. Am. Chem. Soc., 77, 4262 (1955).

(20) K. J. Liska and L. Salerni, J. Org. Chem., 25, 124 (1960).

(21) B. Esch and H. J. Schaeffer, J. Am. Pharm. Assoc. Sci. Ed., 49, 789 (1960), C. A., 55, 6404 (1961).

(22) C. van der Stelt and W. Th. Nauta, Arzneimittel Forsch., 7 278 (1957), C. A., 51, 13812 (1961).

(23) Sabatier and Reid, op. cit., p. 205.

wise first to phenyl propionic acid and then to cyclohexyl propionic acid, thus indicating that a double bond was more easily reduced than a phenyl group and was preferentially adsorbed on the catalyst.

Sheridan and Reid (24) used rhodium to reduce acetylene to ethylene and ethane. About twenty per cent of the original acetylene was converted to a partly hydrogenated polymer. Dunworth and Nord (25) hydrogenated a variety of carbon-carbon double bonds with five per cent rhodium on alumina.

The double bonds in rosin acids and rosin acid derivatives were reduced over rhodium (26) with negligible degradation of the original compound. Green and Cohen (27) have reduced cytosine to dihydrocytosine, citidine to dihydrocytidine, and deoxycytidylic acid to dihydrouredylic acid using a rhodium catalyst.

Rhodium has also been used for a variety of reductions other than benzene nuclei and isolated carbon-carbon double bonds. Sylvan, 2-methylfuran, was reduced (28) over rhodium on carbon at 200° C. to a mixture of 40 per cent tetrahydrosylvan and 60 per cent 2-pentanone. At 300° C.

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(24) J. Sheridan and W. D. Reid, J. Chem. Soc. (London) 1952, 2962.

(25) W. P. Dunworth and F. F. Nord, J. Am. Chem. Soc., 74, 1459 (1952).

(26) A. L. Glasebrook, A. N. Hoffmann, and J. B. Montgomery, U. S. Patent, 2,776,276 (Jan. 1, 1957), C. A., 51, 6185 (1957).

(27) M. Green, and S.S. Cohen, J. Biol Chem., 228, 601 (1957).

(28) N. I. Shuikin, I. F. Bel'skii, Zhur. Obshehei Khim., 29, 1093 (1959). C. A., 54, 1481 (1960).

the product was 100 per cent 2-pentanone. 2-Vinylfuran reduced to ethylfuran at 150° C. (29). Cyclohexanone oxime was reduced (30) to cyclohexylamine with five per cent rhodium on Norite. Some cyclohexanol was produced when aqueous base was used as the solvent. This was attributed to hydrolysis of the intermediate imine and the subsequent reduction of the resulting ketone. The reduction was observed to occur faster in basic solution than in neutral or acidic media.

Nitric acid was reduced to hydroxylamine (31) over rhodium on carbon at 25° C. and 50 p. s. i. g. hydrogen. Copper sulfate was added to depress the activity of the catalyst and thereby prevent the reduction of the hydroxylamine to ammonia.

Dunworth and Nord (32) found that five per cent rhodium supported on carbon reduced quinones and activated nitro, carbonyl, and nitrile groups. Stewart (33) showed that the reduction of a nitro group using rhodium catalyst and acetic acid as solvent proceeded in a stepwise manner.

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(29) Ibid.

(30) E. Breitner, E. Roginski, and P. Rylander, J. Chem. Soc., 1959, 2918.

(31) Spencer Chemical Co., British Patent, 772,670 (April 17, 1957), C. A., 51, 17120 (1957).

(32) Dunworth and Nord, op. cit.

(33) B. B. Stewart, Catalytic Hydrogenation of Nitro Compounds over Supported Rhodium in Acetic Acid--Exchange of Deuterium Gas and Methanol in the Presence of Raney Nickel, Unpublished Ph. D. Thesis, University of Tennessee, 1959, Dissertation Abstracts, 20, 1196 (1959).

Breitner, Roginski, and Rylander (34) studied the reduction of methyl iso-butyl ketone, cyclopentanone, cyclohexanone, mesityl oxide, and acetophenone to the corresponding alcohols as a function of the pH of the solvent and employing five per cent rhodium on carbon. They found that the reduction was faster in basic solutions than in neutral or acidic media. They also observed that cyclohexanone was reduced more rapidly than cyclopentanone, and a phenyl ring was reduced preferentially over a keto carbonyl.

Balandin, Khidekel, and Patrikeev (35) reduced the 1,1-diphenyl-2-picryl-hydrazyl free radical using 0.08 per cent rhodium on alumina. During the reaction the color of the solution changed from violet to brown, indicating the destruction of the radical.

Bond and Newham (36) used a pumice-supported rhodium catalyst to convert cyclopropane to propane. The rate determining step was considered to involve both cyclopropane and adsorbed hydrogen atoms. Similarly, methyl cyclopropane yielded isobutane in high yield.

The mechanism by which rhodium catalyzes the hydrogenation of a carbon-carbon double bond has been studied by Hernandez and Nord (37,38),

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(34) E. Breitner, E. Roginski, and P. Rylander, J. Org. Chem., 24, 1855 (1959).

(35) A. A. Balandin, M. L. Khidekel, and V. V. Patrikeev, Izvest. Akad. Nauk. S. S. S. R., Otdel. Khim. Nauk., 1959, 361, C. A., 53, 19933 (1959).

(36) G. C. Bond and J. Newham, Trans. Faraday Soc., 56, 1501 (1960).

(37) L. Hernandez and F. F. Nord, Experientia, 3, 489 (1947).

(38) L. Hernandez and F. F. Nord, J. Colloid Sci., 3, 363 (1948).

who studied the reduction of the double bond using both a palladium and a rhodium catalyst in which the metal was present in a colloidal form supported on a high molecular weight polymer. As the pH of the solvent increased,the activity of rhodium increased; but the pH had no effect on the palladium catalyst. Compounds which had an electron attracting substituent hydrogenated more rapidly over rhodium than compounds which did not have such groups. The reduction of propylene derivatives was favored by the polarity of the adjacent group, also. These results were interpreted as showing that the mechanism of reduction with rhodium occurred through ionic hydrogen, and the function of the catalyst was considered to be the ionization of molecular hydrogen.

Since the work involved in this research was primarily of a kinetic nature, it seems advisable to discuss the equations and terminology which will be used in later chapters of this thesis.

It is obvious that some reactions proceed with a greater velocity than others. There are situations where it is desirable to know the relative rates of several reactions. It may be sufficient to say that reaction A is faster than reaction B, but often a more precise definition of the relationship is needed. Since many reactions do not proceed with a constant rate, but rather with one that constantly varies, it is desirable to find some way of assigning a value to the rate which represents the overall reaction rate. To this end the study of kinetics has developed general equations which can be applied to most reactions.

It has been observed that many reactions occur at a rate proportional to the concentration of one of the reactants present. Since the

reactant is being used up, the reaction rate constantly changes. Thus, when one half of the original reactant is used up the reaction rate is one-half the original rate. Other reactions may have a rate proportional to some power of the reactant concentration other than one. For the purpose of definition, the reaction rate may be considered to be the rate of change of that substance involved in the reaction. A negative sign signifies that the substance is a reactant while a positive sign indicates that it is a product.

For a typical mechanistic equation

$$aA + bB \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} cC + dD$$

where a, b, c, and d represent the number of times A, B, C, and D, respectively, enters the reaction before or during the rate determining step, and k_1 and k_{-1} are the rate constants for the forward and reverse reactions, respectively, the rate may be expressed as the rate of disappearance of A:

$$\frac{-d[A]}{dt} = k_1[A]^a [B]^b - k_{-1}[C]^c [D]^d . \qquad (1)$$

The terms in brackets, [ ], refer to concentration of the particular substance. A derivative is used because the concentrations are constantly changing with time. Similar rate equations may be set up for B, C, or D; the k_1 and k_{-1}'s for these equations will be identical in value to those in Equation 1.

If the reverse reaction can be neglected (i.e., if k_{-1} can be set equal to zero) Equation 1 becomes

$$\frac{-d[A]}{dt} = k_1[A]^a\,[B]^b \qquad (2)$$

The exponent "a" is defined as the order of the reaction with respect to A. Similarly, "b" is defined as the order of the reaction with respect to B. The overall order of the reaction, n, is defined as the sum of the exponents to which the concentrations of the reacting species are raised:

$$n = a + b\ . \qquad (3)$$

Consider the case where a hydrogenation reaction is first order in hydrogen and zero order in acceptor. Since the hydrogen pressure and not concentration is measured as a function of time it is desirable to express the rate equation in terms of pressure. From the general gas law it can be stated that

$$[H_2] = Z\,P_H \qquad (4)$$

where P_H represents the absolute pressure of hydrogen and Z is a proportionality constant dependent on the volume of the system, the temperature of the gas, etc. Substituting $[H_2]$ for [A] in Equation 2 and setting $a = 1$ and $b = 0$ there is obtained

$$\frac{-d[H_2]}{dt} = k_1[H_2]^1\,[B]^0 \qquad (5)$$

which reduces to

$$\frac{-d[H_2]}{dt} = k_1[H_2]\ . \qquad (6)$$

Substitution of Equation 4 in Equation 6 gives

$$\frac{-d\ (P_H\ Z)}{dt} = k_1\ P_H\ Z, \qquad (7)$$

which, upon rearrangement, yields

$$\frac{-d\ (P_H\ Z)}{P_H} = k_1\ dt\ Z\ . \qquad (8)$$

Integration of this equation between the limits of $P_H = P_o$ at $t = 0$ and $P_H = P$ at $t = t$ gives

$$\ln \frac{P_o}{P} = k_1 t\ Z\ . \qquad (9)$$

Upon conversion to log to the base 10 this gives

$$\log \frac{P_o}{P} = \frac{k_1 t\ Z}{2.303}\ . \qquad (10)$$

Thus a plot of log P_o/P versus time yields a straight line, the slope of which equals $Z\ k_1/2.303$. The apparent rate constant, $k_1 Z$, therefore, may be obtained by multiplying the slope of the line by 2.303. The apparent rate constants must be converted to actual rate constants if the system is changed and comparisons between systems are desired. If the system remains essentially the same with the exception of the volume of the hydrogen supply system, the apparent rate constants may be compared by multiplying them by the volume of the hydrogen to which the pressure measurements apply (39). Thus a reaction having a total volume of one liter of hydrogen present would appear to react at twice the rate of a similar system having a two liter hydrogen volume. Conversion to a true

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(39) H. A. Smith, W. Bedoit, Jr., and J. Fuzek, J. Am. Chem. Soc., 71, 3769 (1949).

rate constant is much more difficult and requires a knowledge of the solubility of hydrogen in the solution being studied.

Now consider a situation in which both the hydrogen and the acceptor concentration contribute to the rate of reaction. If the reaction is first order in both hydrogen and acceptor, Equation 2 becomes

$$\frac{-d\,[A]}{dt} = k_1\,[H_2]\,[B]\ . \tag{11}$$

Let the concentration of H_2 at time t be represented by $a - x$ where a is the original concentration of H_2 and x is that amount reacted at time t. Similarly, let $b - x$ represent the concentration of acceptor at time t. Then Equation 11 becomes

$$\frac{dx}{dt} = k_1(a - x)(b - x) \tag{12}$$

which, in integrated form, is (40)

$$\frac{1}{b - a}\ \ln\frac{a(b - x)}{b(a - x)} = k_1 t\ . \tag{13}$$

This equation is valid only when the stoichiometry of the reaction is one to one. For plotting purposes the equation can be changed to log to the base 10.

$$\frac{1}{b - a}\ \log\frac{a(b - x)}{b(a - x)} = \frac{k_1 t}{2.303} \tag{14}$$

Thus a plot of log $a(b - x)/b(a - x)$ versus t would yield a line with a slope equal to $k_1/2.303$.

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(40) A. A. Frost and R. G. Pearson, Kinetics and Mechanism, Second edition, John Wiley and Sons, Inc., New York, 1961, p. 17.

If one of the components is present in such amount that its concentration does not appreciably change during the course of the reaction the reaction is said to be of a pseudo order. The reaction will appear to be of an order which does not include any contribution from the reactant in excess. Equation 12 can be applied to this situation. Assume that H_2 is present in sufficient quantity so that its concentration does not change appreciably compared to the change in the acceptor concentration. Then $a - x$ becomes a constant. Equation 12 may then be expressed as

$$\frac{dx}{dt} = k' (b - x) \tag{15}$$

which upon rearrangement and integration reduces to a first order equation:

$$\ln (b - x) = k't \tag{16}$$

A plot of log $(b - x)$ versus t yields a straight line of slope $k'/2.303$. It must be remembered that k' is not k_1 since k' is composed of k_1 multiplied by $(a - x)$. Since $(a - x)$ is practically equal to "a" which in turn equals the concentration of H_2, the rate constant obtained from reactions of this sort may change with changing hydrogen pressure. Thus a reaction at 60 p. s. i. g. treated according to Equation 16 may yield a reaction rate constant twice that of an otherwise identical reaction run at 30 p. s. i. g. This may not be observed if the concentration is so great that further increases are not felt by the reaction. If the amount of the pseudo reactant is infinitely large with respect to the other reactants, doubling the amount will not affect the rate since twice infinity is still infinity.

Heterogeneous catalytic reactions, like most chemical reactions, demonstrate a dependence of rate upon the reaction temperature. Therefore, before the reaction rate constants of reactions can be compared they must be converted to the same temperature. To make this correction the activation energy of the reaction must be known. This is found from the reaction rate constants for the reaction at different temperatures.

Quite often the temperature dependence will be such that a plot of log k versus $1/T$ will be quite linear. This result is that predicted by the Arrhenius equation:

$$\frac{d(\ln k)}{dt} = \frac{E_a}{R\,T^2} \tag{17}$$

where R is the general gas law constant, T is the absolute temperature, k is the reaction rate constant, and E_a is called the Arrhenius activation energy. The activation energy bears no relationship to the free energy of the reactants and products, just as there is no relationship between the height of two mountains and the depth of the valley between them. It is best considered as an energy barrier over which the reactants must pass before they can be transformed into product.

The Arrhenius equation (17) can be transformed through integration to

$$\ln K = \frac{E_a}{RT} + \text{Constant} \tag{18}$$

which is equivalent to

$$K = e^{-E_a/RT} . \tag{19}$$

Integration of Equation 17 between the limits k_1 at T_1 and k_2 at T_2 and conversion of the resulting equation to log to the base 10 yields:

$$\log \frac{k_2}{k_1} = \frac{E_a (T_2 - T_1)}{2.303\ R(T_1\ T_2)} \qquad (20)$$

A plot of k versus T according to Equation 19 is an "S" shaped curve having a reasonably straight portion which curves toward a horizontal at both ends. At higher temperatures k approaches a constant value asymptotically. At low temperatures the slope of the line decreases with temperature until $k = 0$ at $T = 0°$ K. (41).

The plot of log k versus 1/T may have a break with two linear portions of differing slopes on each side of the break. This is usually attributed to a change in the mechanism of the reaction at the temperature at which the break occurs (42).

While an Arrhenius type of temperature dependence is the most typical, other relationships may be observed. If the log k versus 1/T plot is not linear and the curvature can not be attributed to a transition between two linear portions of the curve, additional terms may be added to the Arrhenius equation to form a new expression which will give a linear plot (42). Explosions, enzyme reactions, and oxidations of carbon are known to follow other relationships (43).

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(41) Ibid., p. 23.

(42) Ibid., p. 24.

(43) Ibid., p. 22.

CHAPTER II

EXPERIMENTAL

All boiling points, melting points and reaction temperatures reported herein are uncorrected.

Apparatus

The Parr Hydrogenation Apparatus

A series 3911 shaker-type hydrogenation apparatus, purchased from Parr Instrument Company, of Moline, Illinois, was used for the majority of the work reported herein. This apparatus consisted of a shaker assembly and a hydrogen tank connected by suitable valves and tubing. The shaker assembly was composed of a bottle holder mounted so that it could rock back and forth about a point approximately one inch above the top of the bottle and a connecting rod attached to a drive wheel. The bottle was caused to oscillate through a 30 degree arc at a frequency of 220 cycles per minute, thus imparting a sloshing motion to any liquid which was in the shaker bottle.

A hydrogen tank of approximately four liters volume was connected to the reaction bottle through a two way valve and a section of high pressure rubber tubing. This valve was arranged so that one position connected the bottle to the tank and another position exposed the bottle to a vacuum pump. Either or both of these positions could be activated to allow evacuation of the bottle, evacuation of the tank, or hydrogen

to enter the bottle. The hydrogen tank was connected to a cylinder of commercial hydrogen through another valve and suitable tubing. A gauge was provided to measure the hydrogen pressure within the system.

The original gauge supplied with the apparatus was discarded in favor of a six inch Ashcroft Laboratory Test Gauge graduated in 0.25 p. s. i. units. While this gauge was accurate, difficulty in estimating the pressure to the nearest 0.05 p. s. i. introduced some experimental error and this gauge was in turn replaced by a similar gauge graduated in 0.20 p. s. i. units.

The bottles used were standard 500 ml. Parr pressure reaction bottles. The actual capacity of these bottles was approximately 470 ml.

The total volume of the system including the bottle was 4.51 liters (44).

The Manometer

The variation of reaction rate with the change in hydrogen pressure was studied during this work. At gauge pressures of 2 p. s. i. the accuracy of the pressure readings afforded by the pressure gauge became questionable. This difficulty was overcome through the use of a manometer.

The manometer consisted of a mercury filled U-tube of six mm. glass tubing and a meter stick so arranged that the difference in the levels of mercury in the two legs of the tube could be measured. A rubber tube led from one leg of the U-tube to the reaction apparatus

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(44) J. Hecht, The Catalytic Hydrogenation of Quinolines, Unpublished M. S. Thesis, Georgia Institute of Technology, 1950, p. 28.

while the other leg was open to the atmosphere. The entire apparatus was mounted on a suitable stand which held the U-tube vertical.

The Distillation Column

Distillation of solvents used in the hydrogenation experiments and that of most of the ketones was accomplished in a Todd Precision Distillation Assembly manufactured by the Todd Scientific Company, Springfield, Pennsylvania. This column provided for the substitution of various fractionation columns within the column heater assembly. Each of the columns used in this work was three feet long; one was a Vigreux type column one-half inch in diameter; the other was a one inch diameter tube packed with one-fourth inch diameter, single turn, glass helices.

The Spectrophotometer

The infrared spectra of the products of hydrogenation were taken using an Infracord Model 137 Spectrophotometer manufactured by the Perkin-Elmer Corporation of Norwalk, Connecticut.

Miscellaneous Equipment

In addition to the major equipment listed above, several pieces of minor equipment were used.

The reactions were timed by a Precision Scientific Company electric timer which was graduated in 0.1 second intervals.

A vacuum pump was needed to evacuate the reaction bottles prior to reaction. This necessitated the use of a filter to remove any of the solvent vapors (usually acetic acid). The filter consisted of four tubes approximately one inch in diameter and one foot long. They were joined in such a manner that the vapors passed through all four in succession.

The first two tubes were packed with soda lime and the second two were packed with potassium hydroxide pellets.

Reagents

Solvents

Ethanol. Commercial solvent grade 95 per cent ethanol was used without further purification.

Acetic Acid. Reagent grade acetic acid purchased from duPont was redistilled through the Todd Apparatus. Both the Vigreux and the helices packed columns were used.

Hydrogen

The hydrogen gas was supplied in cylinders by the National Cylinder Gas Company of Atlanta, Georgia, and was used without further purification.

Catalyst

The catalyst used in all experiments consisted of five per cent rhodium supported on alumina, and was purchased from Baker and Company, Incorporated (now known as Englehard Industries, Incorporated) of Newark, New Jersey. Two lots of catalyst were purchased: the first bore Baker lot number 3877, the second Englehard number 6044.

Ketones

The majority of the ketones used for reduction were purified by the method of Fieser (45) from commercially available ketones. Fieser's method consisted of refluxing the ketone with an excess of potassium

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(45) L. F. Fieser, Experiments in Organic Chemistry, D. C. Heath and Co., New York, 1955, p 281.

permanganate to oxidize any alcohol present, drying over anhydrous calcium sulfate or magnesium sulfate, and distilling the dry material. The boiling points of the purified ketones are listed in Table 1.

Acetone. One liter of commercial solvent grade acetone was purified by the method of Fieser and distilled through the Todd Apparatus equipped with the Vigreux column.

Methyl ethyl ketone. One kg. of Eastman white label 2-butanone after purification by the method of Fieser was distilled using the Todd Apparatus equipped with the Vigreux column.

Methyl n-propyl ketone. Five hundred grams of Eastman practical grade 2-pentanone was purified by the method of Fieser. The dried mixture was distilled through a one foot long, one-half inch diameter, Vigreux column.

Methyl n-butyl ketone.* Methyl butyl carbinol was prepared via the n-butyl Grignard coupled with acetaldehyde, and was oxidized to the ketone with chromic acid. The resulting mixture was dried and distilled through a 12 inch Vigreux column.

Methyl amyl ketone. Two hundred ml. of Eastman white label 2-heptanone was treated according to Fieser's method and distilled through the Todd Vigreux column.

Methyl n-hexyl ketone. Three hundred ml. of Eastman 2-octanone was purified via Fieser's method followed by distillation through a one-half inch diameter Vigreux column one foot in length.

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*The preparation of methyl n-butyl ketone appears in the Appendix.

Table 1. Boiling Points of Ketones

Ketone	Observed B. P. °C./mm.	Reported B.P. °C./mm.	Reference
Dimethyl	54.8/741	56.3	(46)
Methyl ethyl	80.0/746	80.6	(47)
Methyl n-propyl	100.6-100.8/739	101.7	(48)
Methyl n-butyl	126.5/741	127	(49)
Methyl n-amyl	148.6/743	151-152	(50)
Methyl n-hexyl	171.0/743	171-171.5	(51)
Methyl n-heptyl	192-193/741	194.5-195.5	(52)
Methyl n-octyl	208.0/740	211	(53)
Methyl n-nonyl	230.5/744	231.5-232.5	(54)
Methyl iso-propyl	92-92.6/741	93.5	(48)
Methyl iso-butyl	114.0/743	114	(49)
Diethyl	100.5-101.0/749	102.7	(48)
Ethyl n-butyl	145.4-145.6/743	147-148/742	(50)
Cyclopentanone	128.0-128.2/746	130-130.5	(55)
Cyclohexanone	152.2-152.6/743	154.5-154.6	(56)

(46) M. M. Richter, Lexikon der Kohlenstoff-Verbindungen, Dritte Auflage, Teil 1., Verlag von Leopold Voss, Hamburg, 1910, p. 84. (47) Ibid., p. 141. (48) Ibid., p. 237. (49) Ibid., p. 359. (50) Ibid., p. 583. (51) Ibid., p. 851. (52) Ibid., p. 1168. (53) Ibid., p. 1517. (54) Ibid., Teil 2, p. 1882. (55) Ibid., Teil 1, p. 227. (56) Ibid., p. 342.

Methyl n-heptyl ketone.* Acetaldehyde was coupled with the Grignard obtained from n-heptyl bromide, hydrolyzed, and the product was oxidized to the ketone with chromic acid. The ketone was dried and decolorized prior to distillation through a one-half inch Vigreux column one foot in length.

Methyl n-octyl ketone.* A Grignard was prepared from n-octyl bromide, coupled with acetaldehyde, and hydrolyzed. The resulting alcohol was oxidized to the ketone with chromic acid. The dried ketone was purified by distillation through a one-half inch diameter, one foot long Vigreux column.

Methyl n-nonyl ketone. Two hundred g. of Eastman practical grade 2-hendecanone was treated according to the method of Fieser. Distillation was attempted under vacuum but foaming precluded the distillation. The ketone was distilled at atmospheric pressure using the Todd Apparatus and the helices-packed column. The foaming still occurred but the helices and the length of the column combined to keep it under control.

Methyl iso-propyl ketone. Two hundred ml. of Eastman white label methyl iso-propyl ketone was distilled through the Todd Apparatus and the Vigreux column after being purified by Fieser's method.

Methyl iso-butyl ketone. Eastman methyl iso-butyl ketone (100 ml.) was treated by the standard procedure and distilled through the Vigreux column of the Todd Apparatus.

Diethyl ketone. Eastman white lable 3-pentanone was purified by the standard method and distilled through the Todd Apparatus using

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*The preparations of methyl n-heptyl and methyl n-octyl ketones appear in the Appendix.

the Vigreux column. The reductions of the resulting ketone were not satisfactory so the ketone was redistilled. This had no effect upon the reductions indicating that the contaminating material could not be removed by ordinary fractionation. The remaining ketone was placed in a reaction bottle with ten grams of the rhodium-alumina catalyst and this mixture was placed under vacuum and shaken over night on the Parr apparatus. The catalyst was removed by filtration and the reduction of the ketone was tested. The ketone was found to be reduced normally.

Ethyl n-butyl ketone. Two hundred g. of Eastman 3-heptanone was heated with permanganate according to the method of Fieser and distilled on the Todd Apparatus equipped with the helices-packed column.

Cyclopentanone. Three hundred g. of Eastman white label cyclopentanone was treated by the standard method and distilled through the Todd Apparatus equipped with the one inch helices-packed column.

Cyclohexanone. Five hundred ml. of cyclohexanone supplied by Matheson, Coleman, and Bell was treated according to the method of Fieser and distilled through the Todd Apparatus using the helices-packed column.

Procedure

Preparation for Hydrogenation

One of the critical parts of the experimental work was cleanliness. The ability of small amounts of foreign materials to poison the catalyst system used was found to be quite great. Thus the precautions taken to preclude the entry of foreign materials into the system were extensive.

The hydrogen tank was washed with water and then with methanol, and after a drainage period, was placed in a drying oven at 105 °C. to remove all traces of methanol and water. The rubber tubing which connected the tank and the reaction bottle was boiled in strong potassium hydroxide solution for one hour, rinsed, boiled in tap water for another hour, rinsed again, and finally boiled in distilled water for an additional hour. The rubber stoppers which served as closures for the reaction bottles were treated in a similar manner.

When not in use, the system was kept sealed at all times. Hydrogen pressure or a vacuum was maintained within the system during these times. Hydrogen pressure was found to be better for this purpose because it reduced the amount of corrosion caused by residual acetic acid.

The bottles were thoroughly scrubbed in a synthetic detergent and rinsed in tap water. This was followed by chromic acid cleaning solution and a final triple rinse in distilled water. After the bottles were dried in an oven at 105 °C., they were allowed to cool and capped with aluminum foil until needed.

All other glassware used, such as graduated cylinders, pipettes, and syringes was subjected to the same cleaning process. The solvent and reagents were stored in bottles which were also cleaned in this manner.

Hydrogenation Procedure

The general method of hydrogenation included: measuring and introducing the solvent into the reaction bottle; measuring and introducing the ketone into the reaction bottle; weighing the catalyst and

introducing it into the reaction bottle; placing the bottle in the apparatus; and finally, hydrogenating the sample.

The solvent was measured with a graduated cylinder. The usual volume of solvent was 50 ml.

The ketone was measured with either a pipette or a syringe, and was introduced directly into the bottle from the measuring device.

The catalyst was weighed to the nearest tenth of a milligram on a tared watch glass to minimize errors due to bouyancy of the air, etc. After weighing, the catalyst was transferred from the watch glass into the reaction bottle with the aid of a camel hair brush used only for this purpose.

Immediately after the catalyst was placed in the bottle a thermometer was placed in the reaction bottle to obtain the initial solution temperature. While the thermometer was reaching equilibrium with the reaction mixture the apparatus was cleaned. This cleaning consisted of washing the hydrogen inlet tube and stopper with methanol, using a pipe cleaner to swab the internal surfaces of the tube. The thermometer reading was noted, the thermometer removed, and the bottle was placed in the bottle holder. The holding fixtures were then securely fastened.

The appropriate valve was opened and the system was evacuated until the solvent boiled. The valves were adjusted to allow hydrogen to enter and then readjusted to evacuate the system again. In this manner the air in the bottle was removed. The above procedure was repeated twice. After hydrogen had been added for the third time the system was considered to be essentially free of air. The hydrogen

pressure was then adjusted to the desired amount and the initial pressure noted at time zero. A timer was started simultaneously with the shaking mechanism. The pressure drop was followed as a function of time.

When the reaction was complete, the shaker and the timer were stopped, the hydrogen pressure released, and the system was again placed under vacuum to remove residual hydrogen from the bottle. After readmitting air, the bottle was opened to the atmosphere, the clamps removed, and the bottle was removed from the apparatus. The final temperature of the solution was taken, and the catalyst was removed from the reaction mixture by filtration. The stopper and inlet tube were cleaned in methanol, again using a pipe cleaner to scrub the interior surfaces of the hydrogen inlet tube. The apparatus was then ready for another run.

Procedure, Rate Constant Versus Hydrogen Pressure Studies

The normal pressure for hydrogenation was 64 p. s. i. a. In addition to this pressure, reactions were run at 32 p. s. i. a. and 16 p. s. i. a. The reactions at 16 p. s. i. a. differed from the other reactions in that a manometer was used to measure the hydrogen pressure.

The reaction mixture was prepared in the usual manner, and the bottle was subjected to the usual treatment to remove residual air. The valves were then closed and the tubing to the vacuum pump was removed. The manometer was connected at the point where the vacuum pump was normally connected, both valves were opened, and the pressure adjusted to the desired value. Instead of measuring the pressure of the system on the gauge, the difference in the height of the mercury in the legs of the manometer was noted. By the use of suitable conversion factors this

could be converted to p. s. i. This method enabled one to obtain a greater degree of accuracy in the measurement of the pressure than could be obtained by using the pressure gauge.

Procedure, Activation Energy Studies

The general procedure for the actual hydrogenation was the same as for a normal hydrogenation. The difference was in the method of obtaining temperature control. Since the Parr has no provision for temperature control, the temperature of the surroundings must be maintained at the reaction temperature. This means that the room in which the apparatus is contained is actually a large air bath.

The temperature of the room was adjusted to the temperature of the reaction and was maintained at that temperature long enough for the reaction bottles, ketone, solvent, and apparatus to reach thermal equilibrium. The temperature range was limited to 15° C. on the low side by the freezing point of the solvent. During the winter low temperatures were easily obtained by leaving the windows open over night. The upper temperature range was in the neighborhood of 40° C. since in this range the vaporization within the system became appreciable and since it was difficult to obtain enough heat input to exceed this figure. The higher temperatures were obtained by closing the doors and windows of the room and lighting burners. A homogeneous temperature was attained by circulating the air with an electric fan. The room temperature could be controlled to within plus or minus one degree.* The central heating system

*The temperature control was shown to be reasonably accurate when data taken using the magnetically stirred apparatus (see Appendix) were identical to that obtained using the Parr.

of the building could also be used during that part of the year when it was in use. The steam lines were used for some of the higher temperatures but this resulted in a very high relative humidity and consequently caused problems in weighing the catalyst.

Product Isolation and Identification

The catalyst was removed from the reaction mixture by filtration through a fritted glass disk. After cooling to 0° C., the acetic acid was neutralized by adding cold, concentrated KOH until the phenolphthalein endpoint was reached. Three extractions with ether were made and the extracts were washed with cold water. The ether layer was dried over anhydrous magnesium sulfate and filtered. Removal of the ether by distillation yielded a crude product which was purified by fractionation through a six inch long, one-fourth inch diameter, Vigreux column.

The products were identified by boiling points, derivatives, and comparisons of infrared spectra to those of known alcohols.

CHAPTER III

DISCUSSION OF EXPERIMENTAL RESULTS

Acetone was chosen as a standard hydrogen acceptor and was therefore investigated extensively. The remaining ketones studied were chosen for their structural characteristics which would make a relationship of ketone structure to hydrogenation performance most likely to appear. The products of reaction were shown to be the corresponding alcohols (See Table 2). The products of the reductions of methyl n-butyl, methyl n-heptyl, and methyl n-octyl ketones were not isolated.

The work was divided into six broad catagories:

a. The kinetics of the reaction;

b. The relationship between the reaction rate constant and the concentration of ketone present;

c. The relationship between the reaction rate constant and the initial hydrogen pressure;

d. The relationship between the reaction rate constant and the amount of catalyst used;

e. The relationship between the reaction rate constant and the reaction temperature; and

f. The relationship between the reaction rate constant and the structure of the ketone.

No attempt was made to study each ketone for its behavior in all catagories. Table 3 will illustrate the studies made and the ketones upon which they were made.

Table 2. Products of Hydrogenation

Alc. Exp. Carbinol	Obs. B. P. °C./mm.	Rpt. B.P °C./mm.	Reference	Remarks
Dimethyl	80.1/740	82.5	(57)	I. R. identical to known
Methyl ethyl	97.0/739 (micro)	99/738	(58)	I. R. identical to known
Methyl n-propyl	117.0/740 (micro)	118.5/753	(59)	3,5-dinitro-benzoate, m. p. 61-61.5; reported,62°,(60)
Methyl iso-propyl	112.0/742	112.5	(61)	α-naphthyl urethan, m.p. 107-107.5°; reported,109°,(60)
Methyl iso-butyl	129/742	131	(62)	I. R. identical to known
Methyl n-amyl	155.1/740	156-7/762	(63)	3,5-dinitro-benzoate, m. p. 48-48.6°; reported 49°, (64)
Methyl n-hexyl	174/740	177.6-177.8	(65)	3,5-dinitro-benzoate, m. p. 31-31.4°; reported 32°, (66)
Methyl n-nonyl	227/743	231-2	(67)	

continued next page

Table 2 - continued

Alc. Exp. Carbinol	Obs. B. P. °C./mm.	Rpt. B. P. °C./mm.	Reference	Remarks
Diethyl	113.4/740	116.5/758	(59)	α-naphthyl urethan m. p. 71°, reported 71°, (60)
Ethyl n-butyl	151.6/740	156.5-157/750	(68)	
Cyclopentanol	137/739	139	(69)	I. R. identical to known
Cyclohexanol	156.6/739	160-161	(70)	I. R. identical to known

(57) Ibid., p. 87. (58) Ibid., p. 146. (59) Ibid., p. 245. (60) N. D. Cheronis and J.B. Entrikin, Semimicro Qualitative Organic Analysis, Second Edition, Interscience Publishers, Inc., New York, 1956, p. 567. (61) Richter, op. cit., p. 245. (62) Ibid., p. 372. (63) Ibid., p.593 (64) Cheronis and Entrikin, op. cit., p. 568. (65) Richter, op. cit., p. 861. (66) Cheronis and Entrikin, op. cit., p. 570. (67) Richter, op. cit., Teil 2, p. 1885. (68) I. Heilbron, Dictionary of Organic Compounds, Oxford University Press, New York, 1946, p. 22. (69) Richter, op. cit., Teil 1, p. 358. (70) Ibid., p. 236.

Table 3. Ketones and Parameters Studied

Ketone	Effect of varying the:			
	Catalyst Amount	Ketone Concentration	Hydrogen Pressure	Reaction Temperature
Acetone	X	X	X	X
Methyl ethyl	X	X	X	X
Methyl n-propyl		X	X	X
Methyl n-butyl				X
Methyl n-amyl				X
Methyl n-hexyl	X			X
Methyl n-heptyl				X
Methyl n-octyl				X
Methyl n-nonyl		X		X
Methyl iso-propyl				X
Methyl iso-butyl				X
Diethyl				X
Ethyl n-butyl				X
Cyclopentanone				X
Cyclohexanone				X

The discussion will be arranged by ketones according to the work done in each of the catagories studied. Thus all work done in each catagory will appear before the next catagory is considered.

The Kinetics of the Reaction

Acetone

Reaction mixtures consisting of 50 ml. of glacial acetic acid, 1.000 g. of catalyst, and 0.0274 moles (2.00 ml.) of acetone were prepared and reduced according to the procedure discussed in Chapter II. The reaction data were processed and a plot of log P_o/P versus time was prepared. This method of plotting kinetic data would be expected to give a straight line if the reaction were first order in hydrogen pressure. Figure 1 represents a typical plot of this type. The expected linearity was not observed. The data were reprocessed and plotted as log $(C_o - x)$ versus t where C_o was the initial amount of ketone and was the amount of ketone present at time t. Figure 2 represents a typical plot of this nature. This was observed to be linear, indicating that the reaction was first order in ketone concentration.

The data indicate that one mole of hydrogen was adsorbed for each mole of acetone present. When the ketone was completely reduced no more hydrogen was taken up upon further shaking.

Ketones Other Than Acetone

The reductions of the ketones other than acetone were all plotted as log $(C_o - x)$ versus t, and straight lines were obtained. This indicated that all of the ketones studied followed a kinetic equation

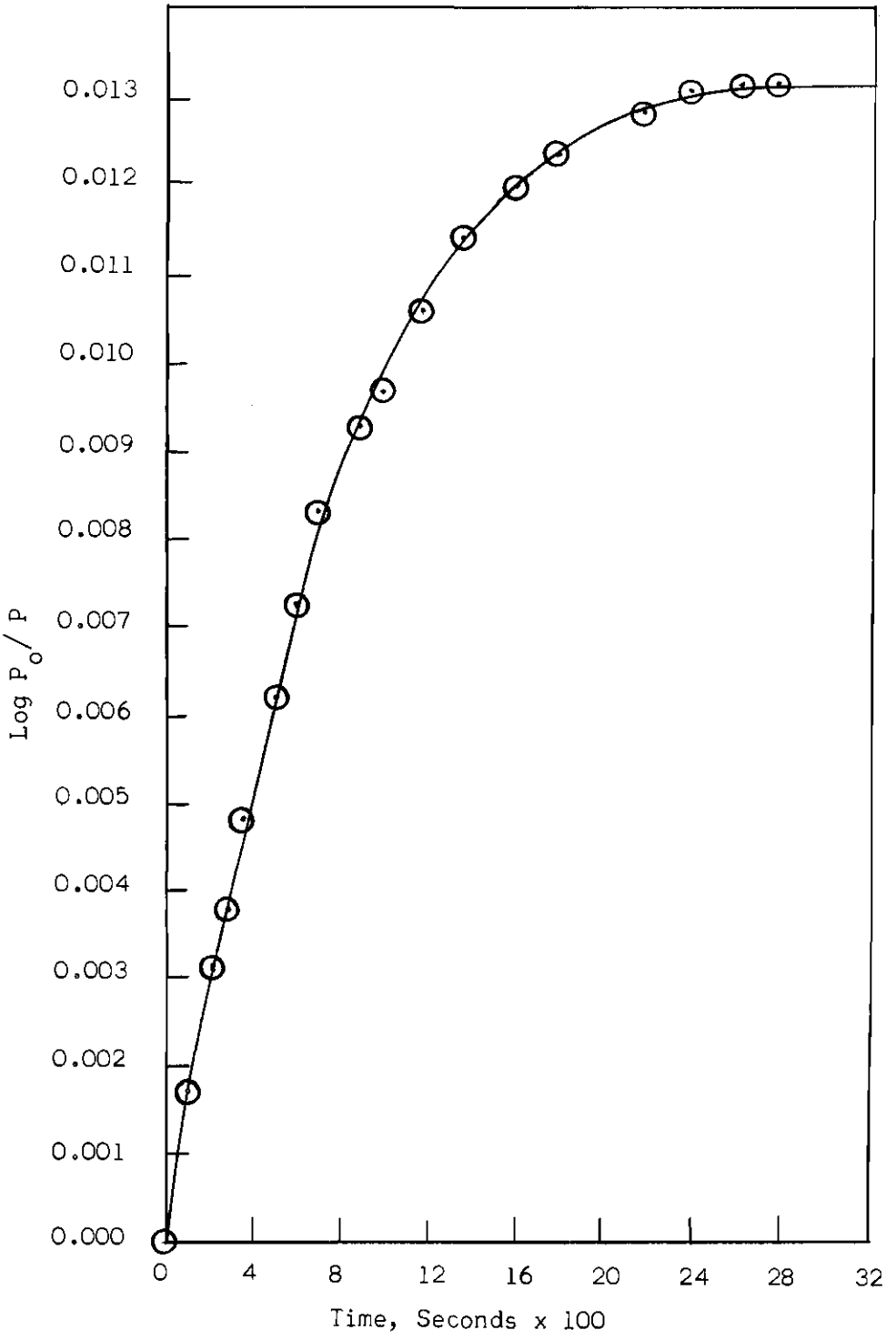

Figure 1. Hydrogenation of Acetone Plotted as First Order in Hydrogen Pressure

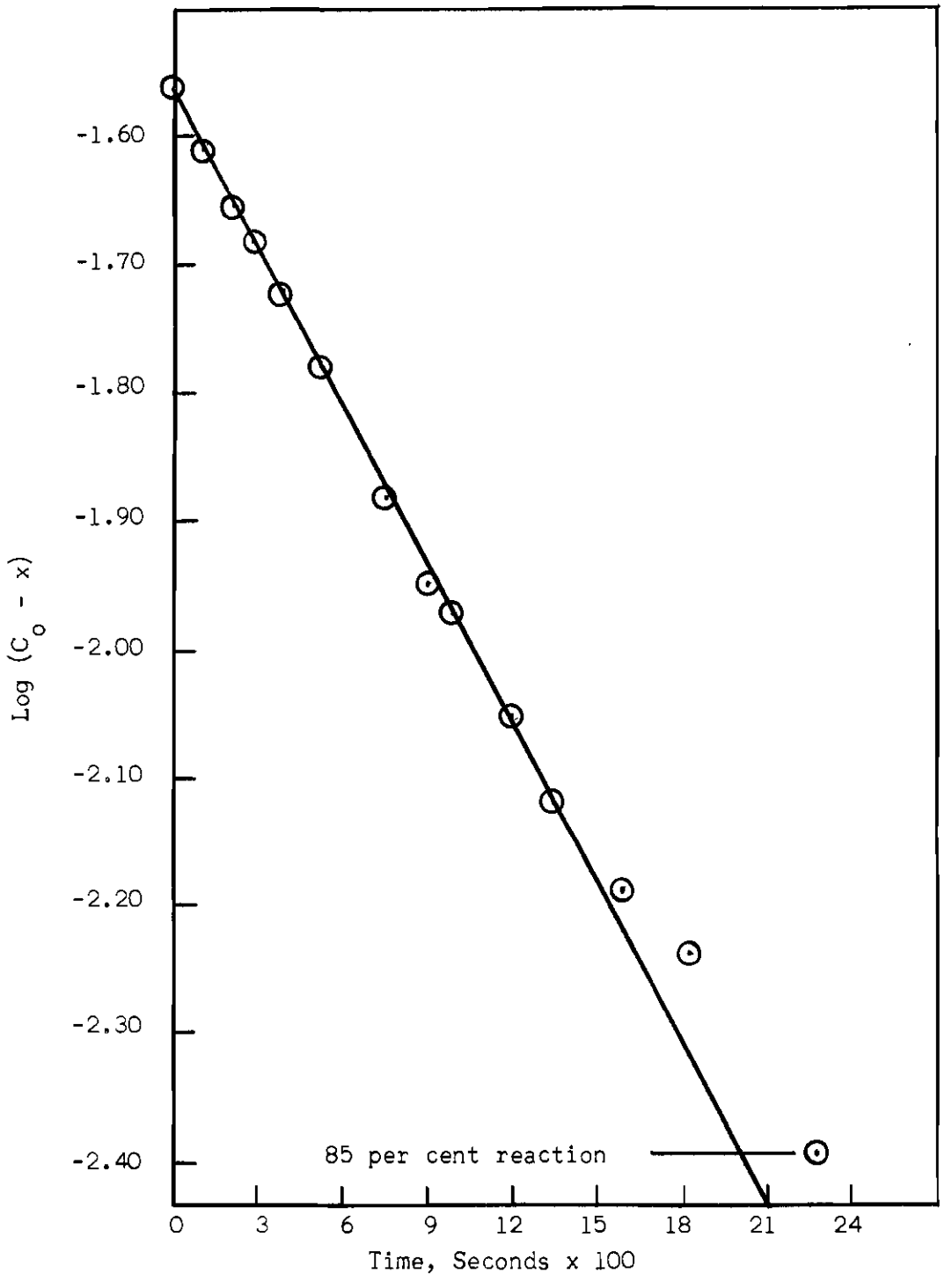

Figure 2. Hydrogenation of Acetone Plotted as First Order in Ketone

representing a reaction first order in ketone. The experimental conditions for these reductions were identical to those for the reduction of acetone.

The Relationship Between the Reaction Rate Constant and the Initial Concentration of Ketone

Acetone

The reaction of acetone and hydrogen was shown to obey a kinetic equation representing first order kinetics with respect to ketone concentration. The reaction rate constant was therefore expected to be independent of the initial amount of ketone used. A series of reductions was made using three initial amounts of ketone. Table 4 shows that the rate constant varied as the ketone concentration changed; indeed, a fourfold increase in the ketone concentration produced a twofold decrease in the reaction rate constant.

Methyl Ethyl Ketone, Methyl Propyl Ketone, and Methyl Nonyl Ketone

The effect noted with acetone was also noted with methyl ethyl, methyl propyl, and methyl nonyl ketone. The data in Table 4 show that here again, the effect of increasing the ketone concentration is a decrease in the reaction rate constant.

The effects summarized in Table 4 indicated that the reaction was not first order with respect to ketone. However, each individual run produced a linear plot when treated as first order in ketone. This conflict put the validity of the original determination of the reaction order in doubt.

Table 4. Initial Ketone Amounts Versus Reaction Rate Constants

Ketone	Moles of Ketone	Reaction Rate Constant	Reaction Temperature
Acetone	0.0137	0.0960 min^{-1}	24.5° C.
Acetone	0.0274	0.0788 min^{-1}	24.5° C.
Acetone	0.0548	0.0580 min^{-1}	24.5° C.
Methyl ethyl	0.0137	0.0965 min^{-1}	27.5° C.
Methyl ethyl	0.0274	0.0706 min^{-1}	27.5° C.
Methyl ethyl	0.0548	0.0561 min^{-1}	27.5° C.
Methyl propyl	0.0274	0.0543 min^{-1}	23.0° C.
Methyl propyl	0.0411	0.0500 min^{-1}	23.0° C.
Methyl propyl	0.0548	0.0460 min^{-1}	23.0° C.
Methyl nonyl	0.0137	0.0534 min^{-1}	21.5° C.
Methyl nonyl	0.0274	0.0377 min^{-1}	21.5° C.
Methyl nonyl	0.0548	0.0184 min^{-1}	21.5° C.

The Noyes equation (71) offers a method of determining the order of a reaction from a knowledge of the fractional lifetimes of the reaction. If the amount of the component whose order is in question can be computed at a given fraction of the time required for the entire reaction, the actual order of the reaction with respect to that compound can be computed. This method can be applied either to a set of reactions by using a varying concentration of the component in question (such as the data in Table 3), or to one reaction by computing the amount of the component in question at various fractions of the lifetime of the reaction.

This equation was applied to data for each individual hydrogenation by computing the ketone remaining at reaction lifetimes of 0.20 and 0.40. The calculations indicated that the reactions were indeed first order in ketone, the average order being 1.05 with respect to ketone. This value is not significantly different from 1.00.

The Noyes equation was then applied to the data in Table 4. The values so obtained are presented in Table 5.

The data of Table 5 probably should be considered accurate to only one significant figure since the half-lives of the reaction are subject to the usual experimental difficulties as well as the additional errors which may be present in the calculations and extrapolations to the half-life. Note that any error in one half-life will tend to cancel out when a series of three reaction half lives versus concentrations are considered. This is the case with methyl propyl ketone.

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(71) Frost and Pearson, op. cit., p. 43

Table 5. Order of the Reaction in Ketone

Ketone	Moles of Ketone for Calculation	Order in Ketone	Average Order
Acetone	0.0548 vs. 0.0274	0.59	
Acetone	0.0548 vs. 0.0137	0.63	
Acetone	0.0274 vs. 0.0137	0.66	0.63
Methyl ethyl	0.0548 vs. 0.0274	0.61	
Methyl ethyl	0.0548 vs. 0.0137	0.56	
Methyl ethyl	0.0274 vs. 0.0137	0.51	0.59
Methyl n-propyl	0.0548 vs. 0.0274	0.62	
Methyl n-propyl	0.0548 vs. 0.0411	0.85	
Methyl n-propyl	0.0411 vs. 0.0274	0.46	0.61
Overall average order for this table			0.62

The reaction order thus appears to be 0.6 in ketone. However, each individual reduction gives a linear plot when treated as first order in ketone. They may be due to competing factors such as the introduction of some term due to hydrogen pressure. Nevertheless, the slopes of the lines of the first order plots can be used to calculate apparent reaction rate constants, and these can be used for comparison purposes. Note that the order of the reaction, as computed by the Noyes equation, does not depend on this apparent reaction rate calculation; it is entirely independent of errors that might be so introduced.

The Relationship Between the Reaction Rate Constant and the Initial Hydrogen Pressure

The reaction was found to follow a linear plot when the log of the concentration of ketone was plotted versus time; the reaction was found not to follow a straight line when log P_o / P was plotted versus t. This indicated that the velocity of the reaction was not influenced by the hydrogen pressure. If this were true, the effect of varying the initial hydrogen pressure would not be observable in the reaction rate constant.

Acetone

Acetone was reduced at pressures of 64, 32, and 16 p. s. i. a. The reductions at 16 p. s. i. a. did not follow the normal straight line when plotted as first order with ketone; neither did they follow a straight line when plotted as first order in hydrogen. These runs were also plotted according to an equation which represented the reaction as first order in both hydrogen and ketone,* and a plot was obtained which was not linear.

The reactions at 64.0 p. s. i. a. had a reaction rate constant of 0.0589 min^{-1} while those at 32.75 p. s. i. a. had one of 0.0386 min^{-1}. The trend is in the expected direction if it is assumed that the reaction is actually first order in ketone. However, from the data at 64.10 p. s. i. a, this reasoning would predict a reaction rate constant of 0.027 min^{-1} for the 32.75 p. s. i. a. reaction.

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*See above, p. 18.

Methyl Ethyl Ketone and Methyl Propyl Ketone

Methyl ethyl and methyl propyl ketone were studied in this respect and the trend observed with acetone was found to be present. In these cases the relationship between the two pressures and the two reaction rate constants was as expected, if the reaction was first order in hydrogen. Table 6 summarizes the data for the dependence of the rate constant on the initial hydrogen pressure.

Table 6. Rate Constant Versus Initial Hydrogen Pressure

Ketone	Initial Hydrogen Pressure	Reaction Rate Constant min^{-1}	Reaction Temperature degrees C.	$K/P \times 10^5$
Acetone	64.10	0.0589	18.5	92
Acetone	32.75	0.0386	18.5	117
Methyl ethyl	63.95	0.101	34.5	158
Methyl ethyl	30.85	0.0499	34.5	162
Methyl propyl	63.70	0.0570	24.0	89.4
Methyl propyl	31.05	0.0276	24.0	88.8

The conclusion drawn from this set of data is that the reaction is first order in hydrogen. The failure of this term to appear in each individual run may be the result of having a relatively small change in hydrogen pressure occurring during the reaction, and a relatively large change in the ketone concentration during the same period. The failure

of the runs at 16 p. s. i. a. to obey the normal kinetic equation may possibly be due to the entrance of a term due to hydrogen into the equation or to the reaction being controlled by diffusion of hydrogen to the catalyst and the rate of shaking.

The Relationship Between the Reaction Rate Constant and the Amount of Catalyst Used

If one considers a heterolytic catalytic reaction as a reaction occurring on the surface of a catalyst, one would expect the reaction to have a rate proportional to the amount of catalyst present. This is found to be true over certain ranges of catalyst amount. At very high relative catalyst weights the catalyst surface may not be utilized efficiently. The rate of reaction can be such that the reactants cannot reach the catalyst surface as fast as they are being adsorbed. This results in a depletion of reactants in the general vicinity of the catalyst and the entire catalyst surface is not able to be covered with reactants. Thus a reaction rate somewhat less than that expected from considerations of the rate at some lower catalyst weight results. The behavior at very low catalyst weights is not fully understood; however, the presence of a larger than normal excess of reactants may effect the equilibrium of the reaction just as the application of pressure to a reaction which proceeds with a change in volume will change that equilibrium. Thus, the ketone may be adsorbed more strongly or the product may be desorbed less readily than when more ideal conditions are observed. At the same time poisoning may exert an effect since the same

amount of poison would be present in both a reaction having a large amount of catalyst and one having only a small amount of catalyst, resulting in a larger percentage of the catalyst being poisoned when a small amount of catalyst was used.

The relationship between the rate and the catalyst weight is often described by a K/g. plot, K being the rate constant at a weight, g., of catalyst. Thus if K/g. is plotted versus g. three situations may arise. The plot may take the form of a horizontal line, indicating that the catalyst is operating under equilibrium conditions; the line may have a negative slope, indicating that the surface is not being entirely used; or the line may have a positive slope, indicating that the catalyst is not present in amounts great enough to allow equilibrium to be reached. The desired portion of the curve is, of course, that portion where K/g. is constant; otherwise small differences in the catalyst weight may cause large discrepancies in the data collected.

Acetone.

The study of the variation of the reaction rate constant with catalyst weight was complicated by poisoning. The studies which were made using small amounts of catalyst were much slower than those which used more catalyst. However, the same amount of catalyst poison could be expected to be in all reaction mixtures. This would cause a larger percentage of the catalyst to be poisoned when small amounts of catalyst were used than when larger amounts of catalyst were used. This made studies useless at catalyst amounts of less than 0.5 g. The experimental error present in the pressure readings was greater, at times, than the

actual pressure drop; a result of the rapidity of the reaction and the small total drop in hydrogen pressure. Table 7 shows the results of this study. The data indicate that the reaction rate was proportional to the amount of catalyst used and thus mean that the reaction was occurring under equilibrium conditions.

Table 7. K/g Versus Catalyst Weight: Acetone. 19° C.

Catalyst Weight, Grams	K/g. min^{-1} $g.^{-1}$
0.500	0.0566
0.600	0.0530
0.800	0.0570
1.000	0.0572
1.100	0.0580
1.200	0.0605
1.300	0.0573
1.400	0.0540
1.500	0.0550
2.000	0.0560
2.500	0.0568
4.000	0.0554
Average	0.0564

Methyl Ethyl Ketone

The above work was repeated using methyl ethyl ketone instead of acetone. The temperature was increased to 30° C. to make the reactions more rapid, decreasing the ratio of the experimental error to pressure drop. The experimental error was reduced by replacing the pressure gauge with a gauge having similar graduations. All runs used 0.0274 moles of ketone and 50 ml. of acetic acid solvent.

Table 8 shows that K/g. was found to be essentially constant over the range of catalyst weights shown, the maximum deviation being less than two per cent.

Methyl Hexyl Ketone

A similar study was made using methyl hexyl ketone at 19° C. The results of the study are given in Table 8 along with data on methyl ethyl ketone. There was a definite tendency for the K/g. for methyl hexyl ketone to increase as the weight of the catalyst was increased. This may be due to a percentage poisoning effect, since the data indicated that the catalyst was being poisoned.

To summarize, these data indicated that the reaction rate was proportional to the weight of the catalyst used and therefore the reaction was occurring under conditions of equilibrium between catalyst and adsorbed and desorbed molecules.

Table 8. K/g. Versus Catalyst Weight

Ketone	Grams	K/g.
Methyl ethyl	0.500	0.0899
Methyl ethyl	0.750	0.0910
Methyl ethyl	0.900	0.0917
Methyl ethyl	1.000	0.0908
Methyl ethyl	1.200	0.0901
Methyl ethyl	1.250	0.0921
Average		0.0908
Methyl hexyl	0.750	0.0343
Methyl hexyl	1.000	0.0345
Methyl hexyl	1.500	0.0390
Methyl hexyl	2.000	0.0409
Methyl hexyl	2.500	0.0395
Average		0.0376

Activation Energy* Studies; The Change of the Reaction Rate Constant with Changing Reaction Temperature

The reductions of all ketones studied obeyed an Arrhenius type relationship of rate versus temperature. A typical plot is shown in Figure 3. Activation energies are tabulated in Table 9.

The initial temperatures of the reactions were used as the temperatures for the Arrhenius plot. While it was recognized that the temperature was not constant throughout the reaction and that some average temperature might be a better choice, the reliability and reproducibility of the initial temperature made it the measurement of choice.

The Relationship Between the Reaction Rate Constant and the Structure of the Ketone

Table 10 is a tabulation of the reaction rate constants for all the ketones studied. These were obtained from the Arrhenius Activation Energy plots and thus are an average of all the data taken. A temperature of 30° C. was chosen because it was the approximate mid-point of the data collected.

The variation of rate with structure shown in Table 10 can be explained solely by steric considerations. This has an analogy in the work of Smith and Pennekamp (72) and that of Lozovoy and D'yakova (73) in which the hydrogenation of benzene substituted with various alkyl

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*See above, p. 17.

(72) H. A. Smith and E. F. H. Pennekamp, J. Am. Chem. Soc., 67, 276 (1945).

(73) A. V. Lozovoy and D'yakova, J. Gen.Chem. (U. S. S. R.) 9, 895 (1939), C. A.,34, 388 (1940).

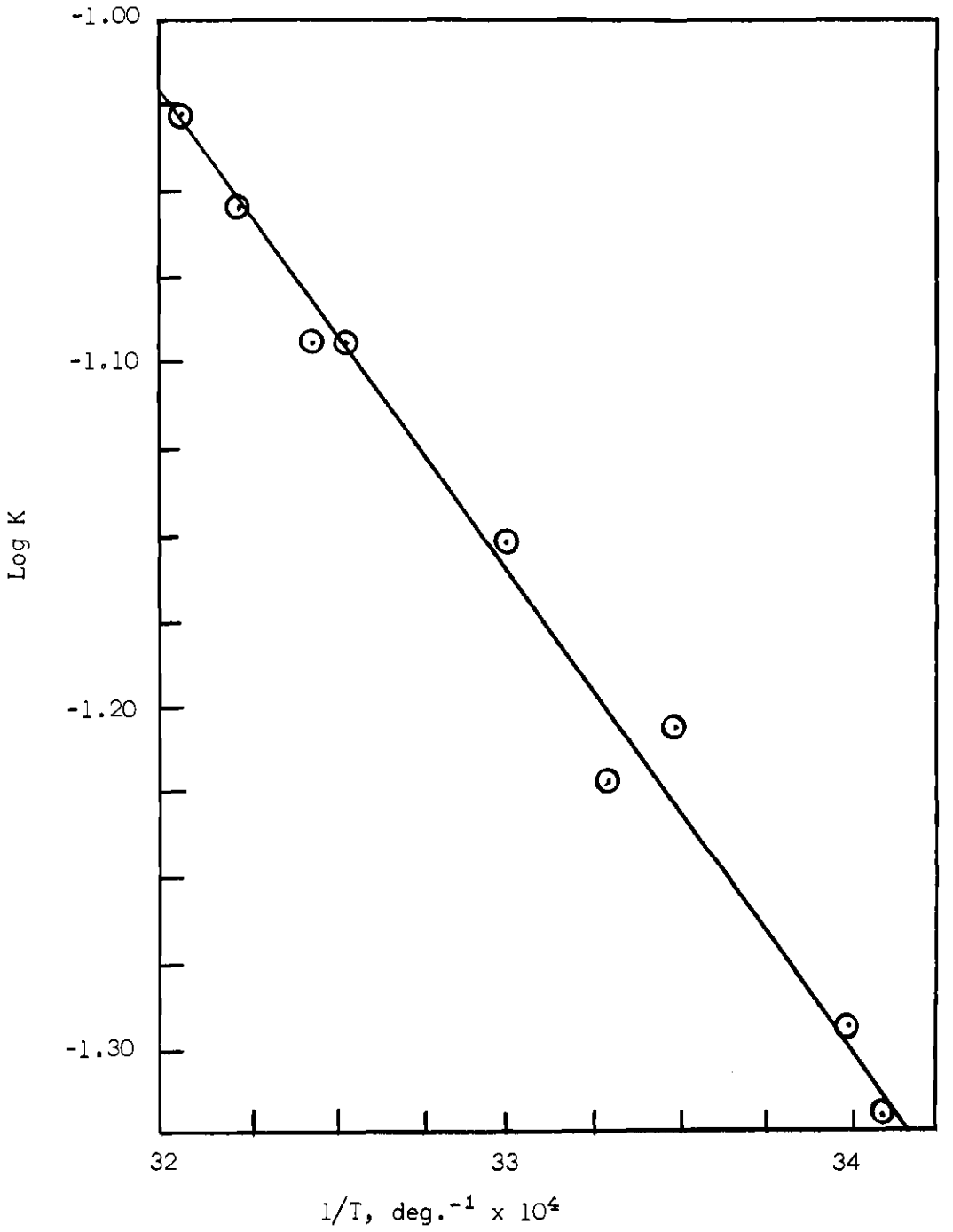

Figure 3. Activation Energy Plot for Methyl Ethyl Ketone

Table 9. The Arrhenius Activation Energy for the Reduction of Ketones

Ketone	Activation Energy Calories
Acetone	7,190
Methyl ethyl	4,240
Methyl n-propyl	6,350
Methyl n-butyl	7,250
Methyl n-amyl	6,040
Methyl n-hexyl	6,010
Methyl n-heptyl	4,570
Methyl n-octyl	6,260
Methyl n-nonyl	3,620
Methyl iso-propyl	11,100
Methyl iso-butyl	10,400
Diethyl	6,340
Ethyl n-butyl	6,380
Cyclopentanone	8,300
Cyclohexanone	8,300

Table 10. Rate Constants for the Reduction of Ketones

Ketone	$K_{30^\circ C.}$
Straight Chains	
Acetone	0.0988 min^{-1}
Methyl ethyl	0.0794 min^{-1}
Methyl n-propyl	0.0686 min^{-1}
Methyl n-butyl	0.0668 min^{-1}
Methyl n-amyl	0.0599 min^{-1}
Methyl n-hexyl	0.0503 min^{-1}
Methyl n-heptyl	0.0483 min^{-1}
Methyl n-octyl	0.0476 min^{-1}
Methyl n-nonyl	0.0479 min^{-1}
Diethyl	0.0657 min^{-1}
Ethyl n-butyl	0.0502 min^{-1}
Branched Chains	
Methyl iso-propyl	0.0102 min^{-1}
Methyl iso-butyl	0.0178 min^{-1}
Cyclic	
Cyclopentanone	0.116 min^{-1}
Cyclohexanone	0.101 min^{-1}

groups was studied. Smith and Pennekamp considered the benzene nucleus to be adsorbed edgewise on the catalyst. The adsorption of a mono-substituted benzene would be prevented at those edges which were adjacent to the substituent, but the adsorption at the other edges would be identical to the adsorption of benzene. Thus, a statistical effect is the only effect noted in a comparison of the adsorption of a mono-substituted benzene versus benzene. This effect would cancel out in a comparison of adsorption of two mono-substituted benzenes; therefore, difference in adsorption could not be responsible for the differences in reaction rate constants.

The substituent effect observed by these workers was considered to be a steric effect on the approach of hydrogen to the catalyst. This can also explain the substituent effect noted in the reductions of ketones reported herein. Table 11 compares the results of these experiments with those on benzenes; for the sake of comparisons the rate constants have been converted to relative rates based on the value of acetone being 100.

Acetone was chosen as a model compound and the remainder of the ketones compared to it. There are two bases of comparison: (a) steric hindrance to adsorption of the ketone on the catalyst surface and (b) steric hindrance to the approach of hydrogen to an appropriate position on the catalyst surface. Comparisons will be made based on the assumptions that: (1) both hydrogen and ketone must be adsorbed before reaction can occur; (2) adsorption of the ketone occurs with breakage of the carbon-oxygen double bond and the formation of a carbon-metal and

Table 11. Relative Rates of Reductions of Ketones as Compared to Substituted Benzenes

Ketone	Relative Rate	Benzene	Relative Rate (72)	Relative Rate (73)
Acetone	100	Benzene	100	100
Methyl ethyl	80.3	Toluene	62	50
Methyl n-propyl	69.5	Ethyl benzene	45	43
Methyl n-butyl	67.7	Propyl benzene	41	45
Methyl n-amyl	60.6	Butyl benzene	38	44
Methyl n-hexyl	51	Amyl benzene	40	41
Methyl n-heptyl	49.1	Hexyl benzene	38	-
Methyl n-octyl	48.1	Heptyl benzene	-	-
Methyl n-nonyl	48.5	Octyl benzene	-	-
		Nonyl benzene	39	-
Diethyl	66.5	(100)*		
Ethyl n-butyl	50.8	(76)*		
Methyl iso-propyl	10.3			
Methyl iso-butyl	18			
Cyclopentanone	106			
Cyclohexanone	102			

*The figures in ( ) compare the relative rates of the two ethyl ketones to diethyl ketone as 100.

an oxygen-metal bond; (3) the resulting adsorbed keto carbon has a tetrahedral rather than a planar structure; and (4) there is sufficient distance between the catalyst and the ketone to allow for rotation of a methyl group.

If a planar acetone molecule approaches the catalyst surface, it will have the least physical interaction with the catalyst when the two methyl groups are eclipsed with one hydrogen on each thrust upward, extending away from the catalyst. As the acetone is adsorbed the methyl groups will "fold back" on each other since the carbon to which they are attached is changing from sp^2 to sp^3 hybridization. This serves to increase the distance between the methyl groups and the catalyst surface. If one hydrogen is replaced with an alkyl group, the alkyl group will occupy the position of one of the "thrust up" hydrogens, and it will present no additional hindrance to the approach of the molecule itself to the catalyst surface. Therefore, any effect on the reaction rate would most likely be due to interference with the approach of hydrogen and not to interference at the catalyst surface.

This hindrance to the approach of hydrogen is clearly not a function of chain length. If that were so, the rates would fall off much more rapidly than they are observed to do. A logical comparison would require some sort of so-called effective size of the groups. This effective size does not lend itself readily to calculation and there appears to be no real knowledge of it. The hydrocarbon chain can coil around into many forms and thus there is some sort of radius that the group can cover. For the purpose of discussion, the group

may be considered to form a lobe which can vary both in length and width as the chain length increases, and which blocks the approach of hydrogen molecules to the catalyst surface accordingly.

The addition of a methyl group to acetone, forming methyl ethyl ketone, increases considerably the size of the lobe which extends away from the catalyst. This size increase may be sufficient to prevent the free rotation of the methyl group around the bound C - O unit to which the substituent is attached. If this is so, the rotation of that methyl group will be restricted to approximately 180° by the physical interaction of the ethyl group with the catalyst bed.

The next addition to form methyl n-propyl ketone will not increase the size of the lobe as much, in proportion, as the first addition did. Consequently the rate constant will not drop as much as it did when the first methyl group was added. From Table 11 it can be seen that this latter addition had about one-half the effect on the rate constant that the first addition had. Thus, the ethyl group may have an effective size of about one and one-half methyl groups.

Further addition of methyl groups tends to increase the length and width of the enclosing lobe in proportionately smaller increments. The blocking effect on approaching hydrogen molecules is, therefore, proportionately less as the length of the chain increases. Chain lengths of seven or more methylene groups appear to have identical blocking effects.

Methyl iso-butyl ketone and acetone have similar structural features which enable each to be adsorbed on the catalyst surface in

equivalent positions. The large size of the iso-butyl group as compared to a methyl group results in a very wide and enclosing lobe which is quite effective in blocking the approach of hydrogen.

Methyl iso-propyl ketone may have some greater degree of interaction with the catalyst surface as it approaches the catalyst prior to adsorption than that observed with the other ketones; but here again, as the group is adsorbed the alkyl groups are moved away from the catalyst. Thus the observed difference in reaction rates is probably due primarily to steric hindrance to the approach of hydrogen. The two methyl groups which extend from the central methyl probably restrict rotation of the central methyl group. This would limit the rotation of that methyl group to approximately 40° or less and thus the blocking group could not rotate out of the way as it can in cases of the straight chain compounds. In view of the restricted rotation, the low relative rate of hydrogenation observed is not surprising.

The ethyl ketone series can be compared with the methyl ketone series since the structure of these ketones would allow them to attain an orientation on the catalyst very similar to that attained by the methyl ketones. Thus differences in the relative rates, both within the series and between the two series, can be attributed to the blocking effect. The effect of adding two methyl groups to acetone, one on each of the existing methyl groups to form diethyl ketone, is approximately twice that observed when one methyl group is added to acetone to form methyl ethyl ketone. Also, the change from diethyl to ethyl n-butyl ketone is of the same approximate magnitude as the effect noted upon

going from acetone to methyl n-propyl ketone. In this latter case the effect of the propyl group on the ethyl ketone is not as great as on the acetone. This is expected when the difference in the distance from the reaction center in the ethyl series is compared to that in the methyl series. The data obtained with the ethyl ketones corroborates the proposition that the reduction in rate observed in the straight chain ketones is primarily due to a blocking effect toward the approach of hydrogen to the reaction center.

The cyclic ketones again may exhibit a different degree of hindrance to the approach of the molecule to the catalyst; but here again, the transition to an sp^3 type structure upon adsorption results in a structure similar to that of adsorbed acetone. The geometry of the rings in both cyclopentanone and cyclohexanone is such that the hydrogens on the carbons adjacent to the carbonyl group are held in one position while the rest of the ring is held back and away from the reaction center. Thus the alkyl portion of the compounds do not hinder the approach of hydrogen. In cyclopentanone, the α-hydrogens are held out of the way of approach of the hydrogen molecules to the surface as compared with acetone. Rotation of the methyl groups of acetone can enable it to attain a similar position but the same rotation will cause the hydrogens to exist in a less favorable structure part of the time. This effect is also present to a lesser degree in cyclohexanone. Here again, the ring forces the hydrogens outward, and all four hydrogens combine to block the hydrogen approach where only two were effective in blocking it in the five membered ring. It is possible to have the ring flip

over into a position which might block the approach but this would probably be a minor effect.

Solvent Effects

The effect of changing the solvent from ethanol to glacial acetic acid was noted as a result of difficulties with hydrogenations using ethanol as solvent. In a comparison of reactions in both solvents using identical amounts of ketone, pressures of hydrogen, and catalyst weights, with both reactions at 21° C., the reduction in ethanol had a rate constant of 200 compared to 300 for acetic acid. Both rate constants are from plots, first order in ketone.

Poisoning Effects

Poisoning was observed to be related to the acetic acid solvent. One reaction might be observed to proceed properly while another reaction, differing from the first only in the batch of acetic acid that was used, would not proceed. Water was thought to be the chief contaminate but the addition of up to two per cent water into the reaction mixture was found to have no effect upon the rate of reduction. The Todd Apparatus was then inspected and found to be heavily contaminated with Dow Corning stopcock grease. A run was made using a known good batch of solvent to which 0.01 g. of Dow Corning Silicone Stopcock Grease was added. This amount of grease was sufficient to stop the reaction completely. This occurred, in all probability, by coating the catalyst with a unimolecular layer of the silicone, thus preventing the adsorption of the reactants.

Cleaning the Todd Apparatus with hot methanolic KOH removed the poisoning material.

Comparison of the Activity of Five per Cent Rhodium on Alumina with PtO_2 for the Reduction of Ketones

Acetone is not reduced by PtO_2 under conditions where rhodium on alumina reduces acetone efficiently.*

*The reduction of acetone was attempted in this laboratory by J. Lowe as part of a research project for a Special Problem course. Subsequent to his failure to reduce the acetone, the same samples of acetone and solvent were reduced by five per cent rhodium in the same apparatus.

CHAPTER IV

CONCLUSIONS

The rate of reduction of alkyl ketones, using a catalyst of five per cent rhodium supported on alumina and a solvent of glacial acetic acid, was found to be directly proportional to hydrogen pressure, 0.6 order in ketone concentration, and directly proportional to the amount of catalyst used. The reactions were found to obey a straight line relationship when plotted according to an equation describing kinetics of first order in ketone.

Glacial acetic acid was shown to be superior to ethanol as a solvent for these reductions.

Dow Corning stopcock grease was shown to be a catalyst poison. Water was observed to have no effect on the reaction rate.

The catalyst under study, five per cent rhodium on alumina, was shown to be more active than platinum black for the reduction of ketones.

The reduction of a series of ketones which differed as to substitution on the carbon adjacent to the carbonyl group demonstrated that the reaction rate was dependent on the size of the substituent. This dependence can be explained on the basis of steric hindrance to the approach of hydrogen to a catalyst site adjacent to an adsorbed ketone molecule.

The temperature dependence of the rate constants of hydrogenation of the ketones was found to obey the Arrhenius equation. The Arrhenius activation energies ranged from 3,600 to 11,100 calories per mole.

CHAPTER V

RECOMMENDATIONS

The magnetically stirred apparatus (See Appendix D) was unable to produce reaction rate constants above 0.040 min^{-1}. While this was tentatively attributed to agitation difficulties, no study was actually made. It seems strange that a reaction first order in ketone and proportional to hydrogen pressure should still give a linear first order plot when the rate was limited by hydrogen diffusion. This appears even more doubtful when the reductions at 16 p. s. i. a. are considered to be limited by hydrogen diffusion and their plots are not straight lines when plotted in the same manner. Therefore, it is recommended that research be conducted into the nature of the limiting factor on rates as observed with the magnetically stirred apparatus.

A P P E N D I C E S

APPENDIX A

PREPARATION OF METHYL n-BUTYL KETONES

Twenty four g. (1 g. atom) of dry magnesium turnings, three small iodine crystals, and 25 ml. of anhydrous ether were placed in a two liter round-bottomed flask equipped with a reflux condenser having a separatory funnel at its top. A solution of 103 ml. (1 mole) of n-butyl bromide in 20 ml. of anhydrous ether was prepared and ten ml. of this solution was added to the flask. Reaction commenced within a few minutes and an additional 25 ml. of dry ether was added as a moderator. After the initial boiling subsided, the remaining solution of n-butyl bromide in ether was added through the separatory funnel at a rate such that the mixture boiled without external heating. Addition was complete in two hours, after which the reaction mixture was placed on a water bath and warmed at a temperature sufficient to cause the ether to reflux gently. After refluxing for 30 minutes, the mixture was cooled in a brine-ice mixture in preparation for the coupling reaction.

Acetaldehyde was prepared by acidifying paraldehyde and distilling the resulting equilibrium mixture. Condensation of the distillate was accomplished by circulating ice water through a cold finger condenser. The acetaldehyde produced was collected in a flask of cold ether surrounded by ice.

Sixty ml. of acetaldehyde in 150 ml. of anhydrous ether was added dropwise to the Grignard solution while the mixture was continuously agitated. The flask remained in the cooling bath during the addition.

After addition was complete, the reaction mixture was allowed to stand at room temperature overnight.

Hydrolysis of the mixture was effected by a mixture of 35 ml. of concentrated sulfuric acid in 300 ml. of water and 300 g. of ice. An ether layer and an aqueous layer formed; the ether layer was separated from the aqueous layer, washed with sodium bisulfite solution, and dried over anhydrous magnesium sulfate after which distillation was attempted. A small iron nail was added to the residue to prevent the explosive decomposition of peroxides which might be present. Degradation of the alcohol in the pot precluded distillation.

By mixing 120 g. of potassium dichromate, 600 ml. of water, and 60 ml. of concentrated sulfuric acid and pouring this into the crude alcohol mixture, oxidation was achieved. The temperature rose rapidly and sufficient cooling was administered to maintain the temperature at 55 - 60° C. for one hour, after which the mixture was allowed to stand overnight at room temperature.

An additional 500 ml. of water was added and the mixture was distilled. The first 200 ml. of distillate was collected as a two layer system. The layers were separated; the water layer was saturated with sodium chloride and extracted with petroleum ether, and the organic layer and the petroleum ether extract were combined. After drying

with anhydrous magnesium sulfate, the organic layer was distilled through a 12 inch long, one-half inch diameter Vigreux column. When the petroleum ether layer had been removed the temperature rose to 126.5° C. at which temperature 29 ml. was collected. The 29 ml. of product represented an overall yield of 24 per cent.

A 2,4-dinitrophenylhydrazone derivative was prepared and was found to melt at 104-6° C. The reported melting point is 110° C. (74).

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(74) Cheronis and Entrikin, op. cit., p. 663.

APPENDIX B

PREPARATION OF METHYL n-HEPTYL KETONE

Twenty four g. (one g. atom) of clean, dry, magnesium turnings was placed in a dry one liter round-bottomed flask equipped with a reflux condenser having a separatory funnel inserted in its upper end. Sufficient ether was added to cover the turnings, and a small crystal of iodine was added to aid in starting the reaction. A solution of 160 ml. (0.87 moles) of n-heptyl bromide in 100 ml. of anhydrous ether was placed in the separatory funnel and ten ml. of this was introduced into the reaction vessel. The flask was warmed slightly to facilitate starting the reaction. After the initial reaction quieted the remainder of the halide solution was allowed to drip into the flask at a rate such that a gentle boiling of the ether was maintained. During the addition the reaction mixture thickened, and it was necessary to add an additional 100 ml. of anhydrous ether. When the bromide addition was completed the reaction mixture was heated on the water bath for 30 minutes.

Acetaldehyde was obtained from a distillation of the equilibrium mixture which resulted upon acidification of paraldehyde.

The Grignard was cooled in a salt-ice mixture and a solution of acetaldehyde and dry ether was added to it dropwise. After the addition of one mole (60 ml.) of acetaldehyde the reaction was observed to be incomplete. This was thought to be true since the addition of more acetaldehyde caused a hissing sound and the appearance of a white precipitate

which redissolved upon stirring, just as earlier additions had produced. An additional 60 ml. of acetaldehyde was added and the reaction appeared to be complete.

The Grignard addition product was hydrolyzed by pouring it into a mixture of 300 ml. of water, 300 g. of ice, and 30 ml. of concentrated sulfuric acid. Two layers formed; the ether layer was separated from the aqueous layer, and the aqueous layer was extracted four times with 50 ml. portions of ether. These extracts were added to the ether layer and the whole dried over magnesium sulfate. The ether was stripped off in the Todd Distillation Apparatus and the remaining material was allowed to cool prior to oxidation.

An oxidation mixture consisting of 120 g. potassium dichromate, 600 ml. of water, and 60 ml. of concentrated sulfuric acid was prepared and poured into the alcohol containing reaction product. The temperature was allowed to rise to 55° C. at which time cooling was introduced to keep the temperature between 55° and 60° C. This temperature was maintained for one hour after which the mixture was allowed to stand overnight. It was then diluted with 300 ml. of water and distilled. The first 200 ml. of distillate was collected as a two layer system, the layers were separated, and the organic fraction was dried over anhydrous magnesium sulfate. Fractionation in the Todd Apparatus equipped with the helices-packed column resulted in 60 ml. of product which boiled at 191-3° C.

Reduction attempts using this material failed to show the presence of a group capable of reacting with hydrogen. Functional group

tests such as 2,4-dinitrophenylhydrazine confirmed the suspicion that the alcohol had failed to oxidize. The boiling points of the alcohol and ketone are not sufficiently different to enable differentiation of the materials; the ketone boils at 194-6° C., the alcohol at 193-4° C.

A new oxidation mixture was prepared from 62 g. of potassium dichromate, 30 ml. of concentrated sulfuric acid, and 300 ml. of water, poured into the alcohol, and the temperature was maintained at 60° C. Two layers formed unless the solution was stirred. A Teflon coated magnetic stirring bar was introduced into the reaction and the vessel was stirred at 60° C. for three hours on a magnetic stirrer-hotplate combination. The solution was allowed to cool and 300 ml. of water was added. Two layers formed. The organic layer was separated from the water layer, the water layer was extracted twice with 50 ml. portions of petroleum ether, and the organic layer was washed three times with 50 ml. portions of a saturated sodium chloride solution. The organic layer and the petroleum ether extracts were combined, and the petroleum ether was stripped off on a steam bath. The remaining material was dried over anhydrous magnesium sulfate and decolorized with charcoal.

The dry, decolorized ketone fraction was distilled through a small, twelve inch long Vigreux column and 27 ml. of ketone boiling at 192-3° C. was collected.

APPENDIX C

PREPARATION OF METHYL n-OCTYL KETONE

Methyl n-octyl carbinol was prepared via n-octyl magnesium bromide which was in turn prepared from 48 g. (2 g. atoms) of dry magnesium turnings and 350 ml. (2 moles) of n-octyl bromide in 350 ml. of dry ether. The magnesium turnings were placed in a dry, two liter, round-bottomed flask and were covered with 100 ml. of dry ether. A magnetic stirrer was employed to stir the mixture while the n-octyl bromide ether solution was added. Three small crystals of iodine were added to the flask and 25 ml. of the halide-ether mixture was introduced. Reaction commenced with rapid boiling of the ether necessitating the addition of 250 ml. of ether as a moderator. A reflux condenser equipped with a separatory funnel at its upper end was attached to the flask and the remainder of the bromide solution was added to the flask through the separatory funnel at a rate which allowed a gentle reflux of the ether from the heat of the reaction. After addition was complete, the solution was allowed to stand overnight.

Since previous Grignard couplings with acetaldehyde apparently resulted in loss of the aldehyde a more direct method of coupling seemed desirable. Accordingly, the usual acetaldehyde preparation apparatus was set up and the column was positioned so that the acetaldehyde produced dropped directly into the Grignard. The flask containing the Grignard was placed in a copper pan filled with ice water, and a magnetic

stirrer was employed to stir the Grignard during the coupling reaction. Acetaldehyde was distilled into the Grignard until further addition produced neither a hissing sound nor the appearance of a white precipitate. The reaction mixture was then allowed to warm to room temperature and stand for one hour.

Hydrolysis was effected by pouring the mixture into 300 ml. of water containing 300 g. of ice and 30 ml. of concentrated sulfuric acid. After separation of the organic layer the aqueous layer was extracted twice with 50 ml. portions of ether and discarded. The combined organic layer and ether extracts were washed with a weak sodium bisulfite solution followed by washings with cold water. A Rotovap dryer was used to remove the ether. Distillation of the mixture yielded 100 ml. of distillate boiling at 210-216° C.

The alcohol was poured into an oxidation mixture consisting of 240 g. of potassium dichromate, 1200 ml. of water, and 170 ml. of concentrated sulfuric acid. The temperature of the solution was maintained between 55° and 60° C. for one hour, during which time the mixture was constantly stirred. At the end of this time heating was discontinued, and the mixture was stirred for an additional three hours.

One hundred ml. of water was added and the resulting layers were separated. The aqueous layer was extracted with two 25 ml. portions of petroleum ether, and the organic layer was washed with 25 ml. portions of a saturated sodium chloride solution. The petroleum ether extracts were added to the washed organic layer, and the resulting mixture was dried over anhydrous magnesium sulfate.

The dried ketone was distilled through a one-half inch diameter, one foot long, Vigreux column. After the petroleum ether was removed, the temperature rose to 208° C. and 46 ml. of 2-decanone was collected.

APPENDIX D

THE MAGNETICALLY STIRRED APPARATUS

The determination of the temperature dependence of the reaction rate constants required some provision for controlling the reaction temperature. The Parr apparatus had no provision for temperature regulation; therefore, an apparatus was constructed with this application in mind.

The apparatus was designed so that the reaction bottles could be placed in a water bath during the reaction. A magnetic stirrer was used to stir the reaction mixture during reduction. This restricted the construction materials to nonferrous materials.

Construction of the Apparatus

The apparatus was designed to use Parr 500 ml. reaction bottles and a Parr hydrogen tank and valves. This not only simplified the construction but provided that the hydrogen system would have a volume identical to a Parr apparatus.

A bottle holder was constructed from two brass plates and two threaded brass rods. The bottom plate was bored one-eighth inch deep to accept the base of a Parr bottle and the enclosing safety shield. Two holes were drilled and tapped in it to accept the threaded brass rods. The upper plate was bored to accept a Parr hydrogen inlet tube and two holes were provided for the passage of the brass rods. Slots

were cut to one of these holes and to the hydrogen inlet tube hole to enable the plate to swing to one side to permit the insertion and removal of reaction bottles without removing the entire top plate. Knurled nuts were provided for the brass rods and were used to apply a compression force between the bottom plate and the top plate, thus holding the stopper in the bottle against the hydrogen pressure.

A watertight tank was constructed in the shape of a cube one foot on an edge. The bottle holder was soldered to the bottom of the tank so that the bottle could be kept in contact with water during a reaction. A magnetic stirrer was positioned under the tank so that the stirring axis was in line with the center of the bottom of the bottle.

A small stirring motor was provided to circulate the bath water and so maintain a homogeneous temperature.

A Parr hydrogen tank and associated valves and tubing were mounted at the rear of the apparatus and connected as was normal for the Parr apparatus. A six inch Ashcroft test gauge was used for pressure measurements.

The reaction bottles were standard Parr 500 ml. pressure bottles modified to provide a better mixing of hydrogen and the reaction mixture. Two baffles were pressed in on diametrically opposite sides of the bottle. These baffles, four inches long and one-half inch wide, created a splashing effect as opposed to the simple vortex obtained in a smooth bottle when the solution was stirred with the magnetic stirrer. A Teflon coated stirring bar was used within the bottle.

Reduction Procedure

The operation of the magnetically stirred apparatus was very similar to that of the Parr apparatus, due in part to the fact that the hydrogen system was identical to the Parr apparatus. The cleaning process was the same for both; the reaction mixture preparation was also the same. The primary difference was in the temperature control.

The bottle containing the reaction mixture was contained within the tank. This tank was filled with water to a point two inches below the top of the bottle. The temperature of the water was adjusted to the desired temperature before the reaction was begun by adding either hot or cold water as required. The stirrer was used to circulate the water in the tank.

A prepared bottle was placed in the bottle holder, the hydrogen inlet tube was secured, and the knurled nuts tightened securely. The system was evacuated in the same manner as the Parr, and the timer and magnetic stirrer were started simultaneously. The rest of the procedure was identical to that followed with the Parr.

Comparisons with the Parr Apparatus

Since the reductions made using this apparatus were to be compared with reductions made using the Parr apparatus, it was deemed necessary to standardize the new apparatus in terms of the Parr apparatus. Also, since the magnetic stirrer had various speed settings, a study of speed versus reaction velocity was needed.

A comparison of the reductions of benzoic acid using platinum oxide and acetic acid solvent obtained on both the magnetically stirred apparatus and on the Parr apparatus, showed that a stirrer speed of eight or more (the stirrer was marked in ten divisions) resulted in identical reaction rate constants for the two machines.

The system was compared to the Parr determined activation energy study of the reduction of acetone and the rates obtained were identical to those observed on the Parr apparatus within experimental error. The activation energy of the reaction was found to have the same value as when determined on the Parr apparatus. However, at higher temperatures, the reaction rate constant failed to increase but instead maintained a constant value for all higher temperatures. This was not observed with the Parr. Since the only real difference in the two machines was in the method of stirring, this phenomenon may be due to stirring being a limiting factor in these instances. The kinetic form of the reaction did not appear to change when this maximum was reached.

Conclusions

These results and the unexplained maximum prompted the decision to abandon this apparatus in favor of the Parr. The correlation of the activation energy determined on this apparatus with that determined using the Parr lends support to the data collected using the Parr.

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VITA

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He was active in the Boy Scout movement, earning the ranks of Eagle Scout and Silver Award Explorer, and the God and Country award. He was elected to the Order of the Arrow, where he earned the Brotherhood Honor. He was a member of Quill and Scroll, a charter member of the Murfreesboro Demolay Chapter, where he served as Master Councilor, and a member of the Phi Sigma Beta honor society. He served as President of the Middle Tennessee State College Chemical Association.

In 1959 he married the former Brenda Faye Douthit. They have two children: Candyce Hardin and Albert Boyd.

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